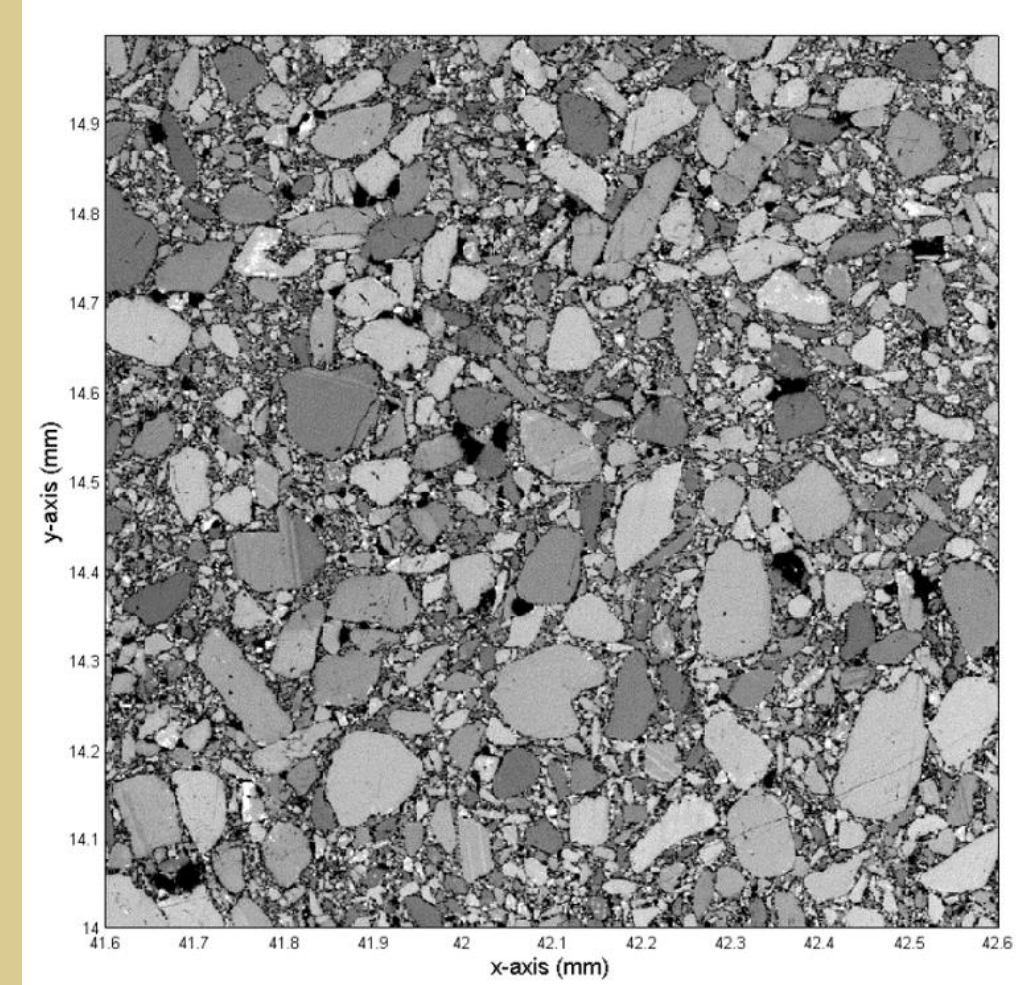


Assessing the suitability of highly filled energetic composites for additive manufacture

Mike O'Donnell, Fracture Group, Cavendish Laboratory, University of Cambridge

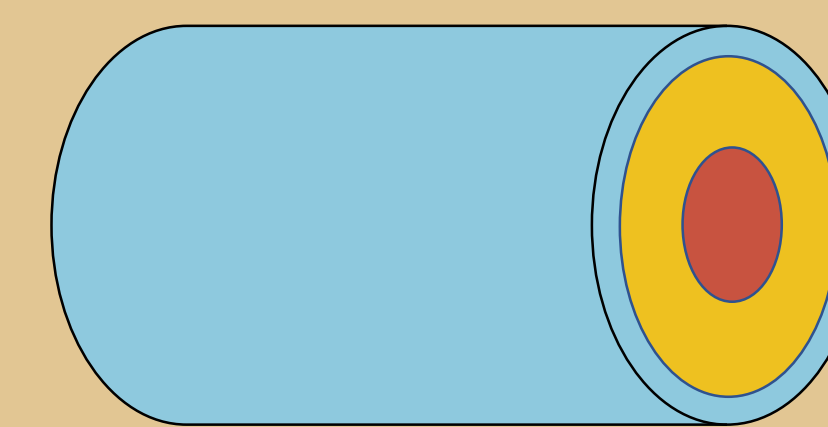
Recent years have seen a huge growth in the use of additive manufacture in various applications, from simple 3D printing of thermoplastics to more complex processes used to form functional parts. There is now a considerable interest in applications of additive manufacture to energetic materials, such as propellants and explosives, as shape and structure can greatly influence their effect. For example, the burning surface of rocket propellants can be tailored by controlling their geometry and additive manufacture techniques could enable production of geometries which are not accessible by conventional means.

Some examples of successful additive manufacture of energetic materials by extrusion have been reported in the open literature, including highly filled propellant formulations^[1]. However, much of this work has focussed on developing specific processes tailored to specific formulations, often using trial-and-error to define suitable conditions and parameters. In order to support more rapid development in this field, it would be desirable to develop a better understanding of how specific properties of these materials interact with additive manufacture processes. This poster provides an overview of the unit processes associated with additive manufacture via material extrusion and discusses how these might affect different energetic composites.

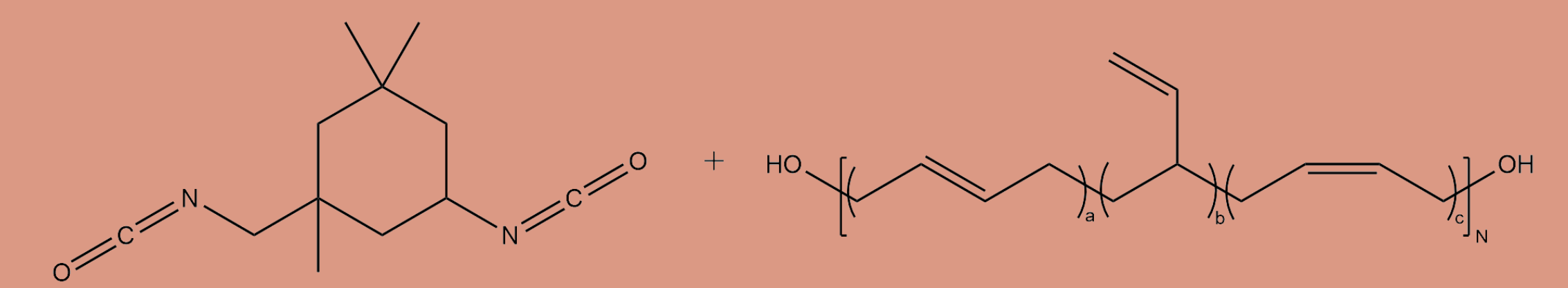


This image shows the microstructure of a modern energetic material, in this case a plastic bonded explosive (PBX). A solid component is dispersed in a polymeric binder system, which is then chemically crosslinked or cured. Formulations of this type are common in explosives and propellants.

The additive manufacture process requires the extrudate or "road" to be laid down on a print bed along a specified tool path. However, it has been reported that the extrusion process can alter the composition of the extrudate. For example, other paste extrusion applications have exhibited a binder-rich slip layer near the die wall^[3] and an annulus of solids-rich material^[4].



The above cross section illustrates some ways in which paste extrusion processes could affect the formation of an extrudate (all dimensions are arbitrary). The blue layer represents a binder-rich depletion layer and the amber layer a solids-rich annulus. Should similar structures be induced in energetic materials, this could profoundly affect the functional and material properties. This could be further studied using, for example, x-ray microtomography or electron microscopy



Energetic composites often require a curing process to assume their final properties. A typical cure reaction is shown above, in which hydroxyl-terminated polybutadiene (HTPB) reacts with isophorone diisocyanate in the presence of heat to form a polyurethane network^[7]. However, alternative chemistries, such as UV curable acrylates could be considered to better integrate with an additive manufacture process.

EXTRUSION

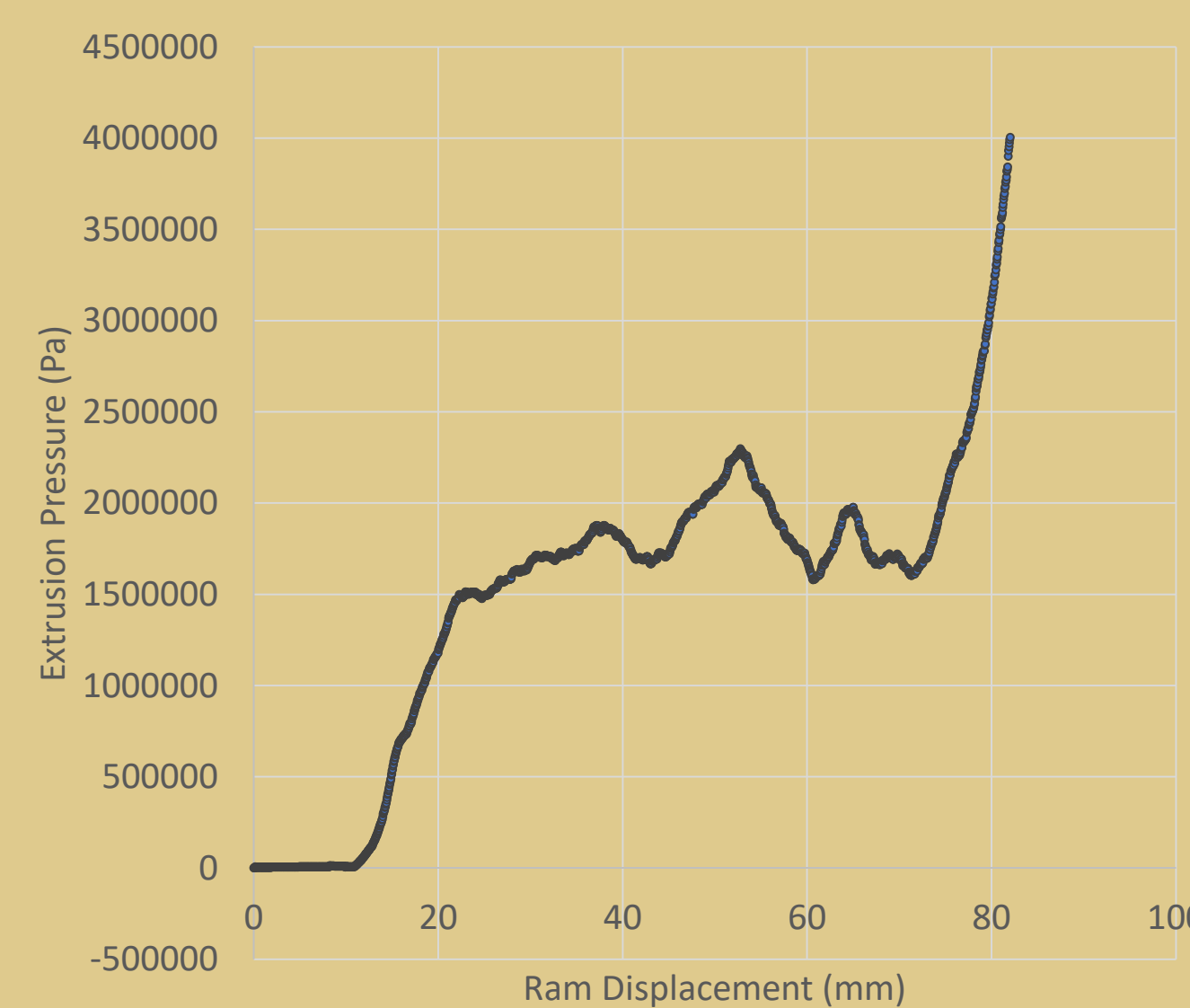
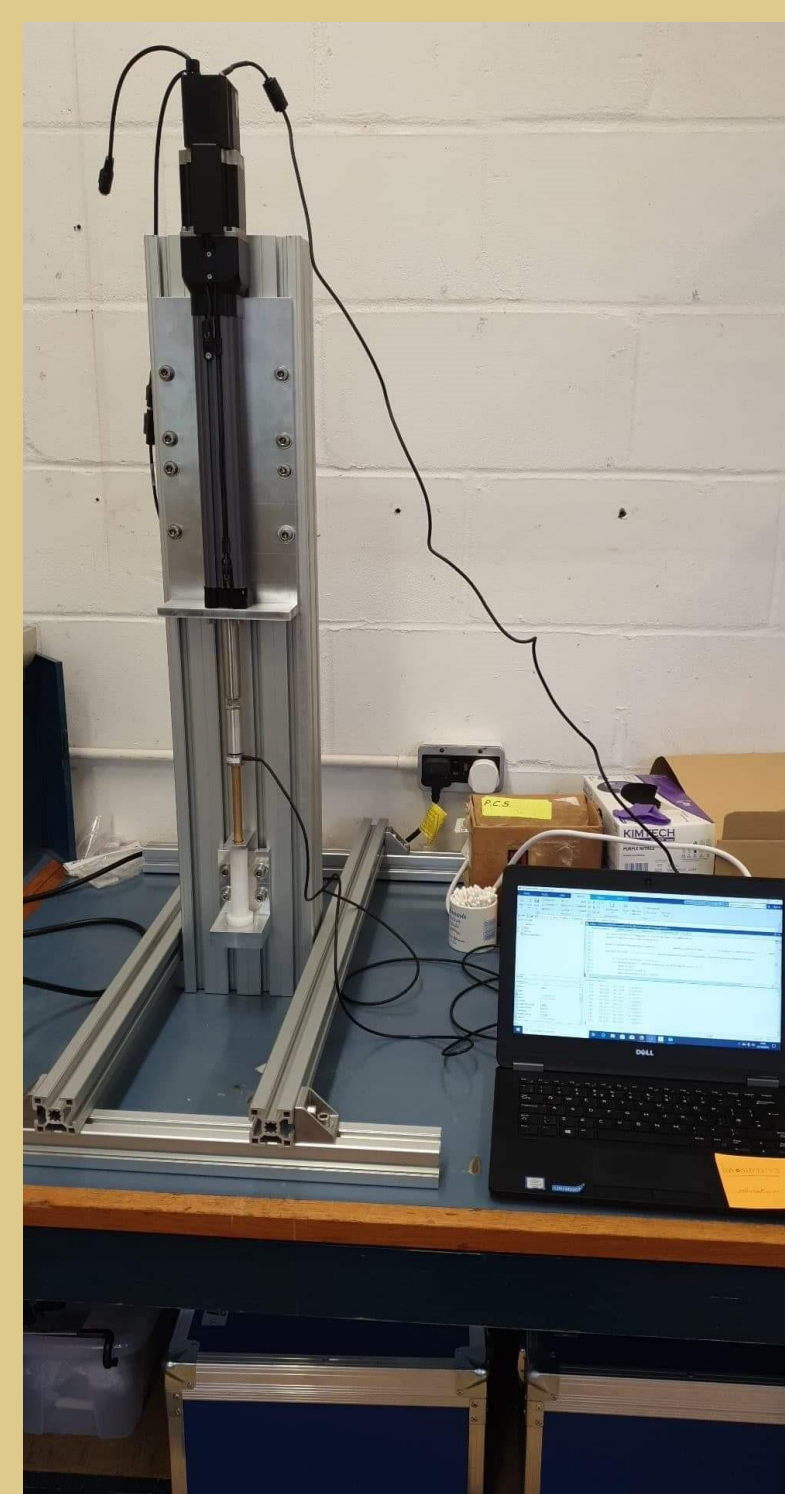
MATERIAL LAYERING

FINISHING

FORMULATION

ROAD FORMATION

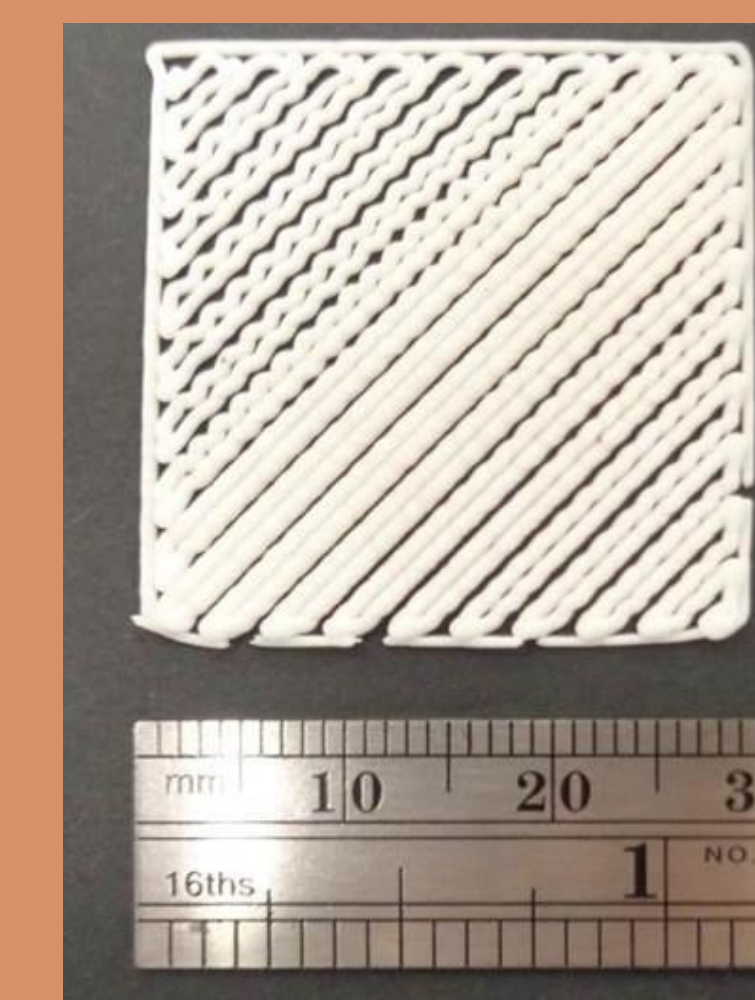
CURING



The adjacent images show an experimental apparatus (left) designed to assess the extrusion of energetic pastes in the Cavendish Laboratory and a plot (above) of extrusion pressure against ram displacement obtained from that apparatus for an inert model material.

In an uncured state, many energetic materials can be considered as pastes. The extrusion of pastes has been studied and a model for paste flow was proposed by Benbow and Bridgewater^[2]. This model relates various aspects of extrusion, including flow rate and pressure, to material-specific parameters which can be assessed experimentally. With some adaptation, this model for paste flow and the associated experimental methods could be used to examine the extrusion of energetics in additive manufacture.

In additive manufacture an extrudate, once formed, is laid down in layers to form the desired object. Informed by an understanding of the extrudate microstructure, it is necessary to consider how adjacent "roads" will interact and whether a sufficient number of layers can be supported. Some approaches to assessing some of these aspects have been reported. For example, the yield stress of the material and layer height can be used to predict a number of layers at which the structure will fail^[5]. The nature of the layer structure would significantly affect the material properties and function of an energetic material. Indeed, anisotropic material properties are often reported in additive manufacture of other material types^[6].



The above image shows a layer of energetic material produced by additive manufacture via extrusion. A number of critical features of the toolpath are evident, including road width, air gaps and raster angle

Ultimately, it is evident that determining the applicability of additive manufacture to energetic composites requires an understanding of how these materials interact with the different unit processes discussed. A number of existing experimental approaches, with some modification, are potentially applicable to this problem. This provides a starting point for further research into this topic.

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